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HIGH PRESSURE AFFECTS ON CONJUGATED AROMATIC COMPOUNDS

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In an effort to determine the affects of high pressure on conjugated aromatic compounds, we have studied the visible spectra of a series of such compounds at high pressure. The series $C_6H_5-(CH=CH)_n-C_6H_5$, where $n=1$ to 4, was chosen for this study. The natural color of these solid compounds changes from colorless to dark yellow as n changes from 1 to 4.

These compounds were subjected to varying pressures in a double ended, opposed diamond anvil press¹⁾²⁾. When observed visually using a microscope, *trans*-stilbene ($n=1$) was observed to change from white to yellow (about 5 kb) to orange (about 50 kb) and contained bright red parts in the center of the anvils at about 85 kb. The other compounds in the series were observed to turn a bright red at a much lower pressure, about 50 kb for 1,4-diphenyl-1,3-butadiene ($n=2$), about 30 kb for 1,6-diphenyl-1,3,5-hexatriene ($n=3$) and about 15 kb for 1,8-diphenyl-1,3,5,7-octatetraene.

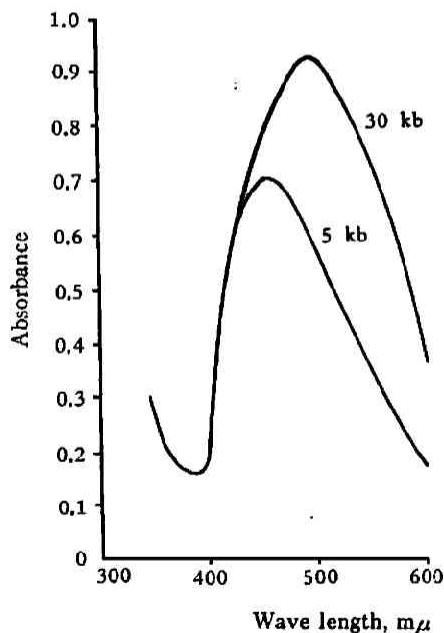


Fig. 1 Pressure spectra of 1,6-diphenyl-1,3,5-hexatriene

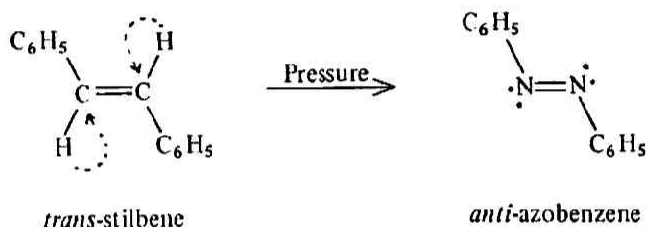
(Received June 1, 1970)

1) W. A. Bassett and T. Takahashi, *Am. Mineralogist*, **50**, 1567 (1965)

2) W. A. Bassett, T. Takahashi and P. W. Stock, *Rev. Sci. Instr.*, **38**, 37 (1967)

The visible absorption of these compounds showed a definite shift to higher wave lengths at higher pressures. 1,6-Diphenyl-1,3,5-hexatriene for example, exhibited a maximum at $470\text{ m}\mu$ at about 5 kb and $500\text{ m}\mu$ at about 30 kb (see Fig. 1). Similar shifts have been observed in the infrared absorption of various compounds^{3,4}. The molar absorptivity could not be calculated due to the fact that solid materials were used and the path length was not known.

On reviewing the above results, one could imagine that high pressure is the alchemical process needed to convert stilbene into azobenzene, one of its isoelectronic counterparts⁵. Thus, high pressure would hypothetically cause the protons to be placed into the nucleus of each carbon atom yielding two nitrogen atoms, since the absorption spectrum of azobenzene is shifted to higher wave lengths with respect to that of stilbene⁶.



The most likely explanation of these results is that high pressure forces the molecules close together so that there is overlap between either the π clouds of the benzene rings or those of the carbon-carbon double bonds. It is well known that as the aromatic hydrocarbons become more condensed (say benzene to anthracene) the absorption shifts to longer wave lengths⁷. In our case the high pressure form could be such that the benzene molecules are acting like condensed systems.

A similar change to longer absorption is also observed in the case of conjugated double bonds. Kuhn synthesized the series of compounds $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_n-\text{C}_6\text{H}_5$ where n varied from 1 to 15. He found that as n increased, the color changed from colorless to yellow, orange, red and finally green-black⁸. When our compounds are subjected to high pressure, a long chain, conjugated π system may be formed. This could explain the color shift.

Work reviewed by Cram⁹ lends some support to the theory that π bond overlap is causing the observed spectral shifts at high pressure. Paracyclophanes showed a definite bathochromic shift when $m=n$ is decreased from 5 to 2. It was calculated that the shift occurred when the distance between

3) J. Osugi and Y. Kitamura, *This Journal*, **35**, 25 (1965)

4) E. R. Lippincott, C. E. Weir, A. Van Valkenburg and E. N. Bunting, *Spectrochim. Acta*, **16**, 53 (1960)

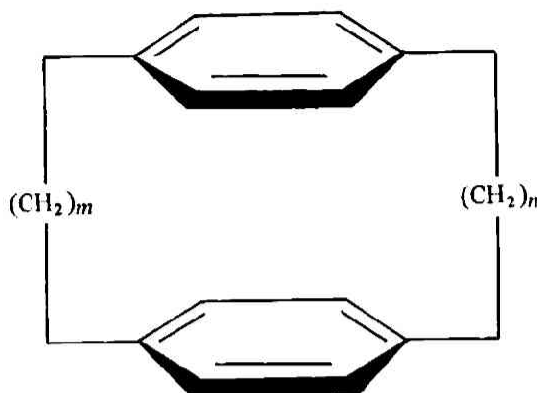
5) For a review of isoelectronic systems and the fact that imaginary alchemical transformations often predict correct results, see H. A. Bent, *J. Chem. Ed.*, **43**, 170 (1966)

6) See H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," pp. 276-282 John Wiley and Sons, Inc., (1962)

7) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949)

8) R. Kuhn, *J. Chem. Soc. (London)*, 604 (1938)

9) D. J. Cram, *Rev. Chem. Prog.*, **20**, 71 (1959)



the rings became less than 3.4 \AA . This means that if under pressure the benzene rings were brought closer together than 3.4 \AA , a definite bathochromic shift would be possible. This process must be an intermolecular process rather than intramolecular since *cis*-stilbene exhibits an ultraviolet spectral shift to lower wave lengths compared to that of the *trans*-isomer⁶⁾.

The spectral shifts that we observed, then, are likely caused by overlap of the π systems. It is undoubtedly a mixture of conjugated double bonds and benzene ring interactions.

Experimental

Materials and apparatus

The organic compounds (*trans*-stilbene, 1,4-diphenyl-1,3-butadiene, 1,6-diphenyl-1,3,5-hexatriene and 1,8-diphenyl-1,3,5,7-octatetraene) were used as purchased from Aldrich Chemical Company. The double ended, opposed diamond anvil press^{1,2)} was purchased from Prof. W. A. Bassett, University of Rochester, Rochester, New York. A Beckman DK-2 spectrophotometer was used to record the visible spectra.

Spectral data

The diamond press was calibrated by observing the phase transitions of silver iodide at 5 kb and 100 kb^{1,2)}. After repeated experimentation, a "feel" for how much force was needed to tighten the press to these pressures and therefore a "feel" for the interval from 5 to 100 kb was established. No specific accuracy is claimed, however; the values are probably no more than 5 kb off on the low end and 10 kb above 50 kb.

Each organic compound was placed in the press and squeezed while the apparatus was in the microscope. Each spectrum was taken when the entire field was yellow or red where possible. This took much care due to the pressure gradient across the anvil^{1,2)}. With stilbene this was not possible due to the high pressure needed. The spectra were obtained by using a blank containing a hole the

same size as the press on the reference beam.

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